

THERMODYNAMICS OF METAL VOLATILITY AND SPECIATION IN THE THERMAL TREATMENT OF ORGANIC-BASED RADIOACTIVE WASTES

Martyn G. Adamson, Bartley B. Ebbinghaus, and Oscar H. Krikorian

University of California, Lawrence Livermore National Laboratory,
Livermore, California 94550, U.S.A.

Chemical thermodynamic data for metal vapor species are required for modeling the behavior of various radionuclides during thermal oxidative treatment (mineralization) of organic-based wastes. Of primary interest are metal volatilization during high-temperature processes such as incineration, and the speciation of metallic waste constituents in innovative organic destruction processes such as molten salt oxidation. We have recently extended our earlier estimates and measurements of $\Delta_f H_{298}^0$, S_{298}^0 and C_p^0 data for U, Pu and Am vapor species by carrying out transpiration experiments on Pu-238 labeled PuO₂(s) in the presence of oxygen and steam. Thus, $\Delta_f H_{298}^0$ is determined to be -562.75 ± 4.95 kJ/mol for PuO₃(g) and $-1,018.15 \pm 3.28$ kJ/mol for PuO₂(OH)₂(g). In applying these new volatility data to an incinerator operating on mixed organic-based wastes, it is found that Pu volatilization makes negligible contributions to air emissions provided the combustion temperature is maintained below 1600 K and F and Cl are absent in the waste. Using the on-line FACT/EQUILIBRIUM computer code and data base, we have also calculated the chemical states of several waste-derived metallic elements at 850 - 950°C in the molten salt (Na₂CO₃) oxidation process. This information has proved valuable in the prediction of vaporization/volatility of species during processing, as well as the development of flowsheets for aqueous processing of spent salt and the selection of containment materials for the molten salt reactor vessel.

This work was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract number W-7405-ENG-48.